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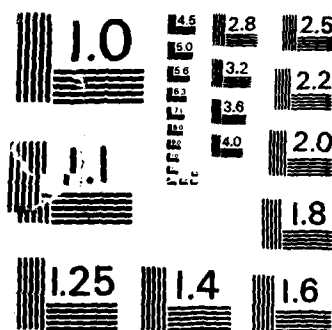
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DISCRETE MODEL FOR INNER-SPHERE REORGANIZATION OF ANIONS

by

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# DISCRETE MODEL FOR INNER-SPHERE REORGANIZATION OF ANIONS

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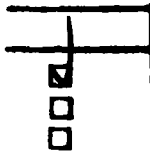
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## 1. Introduction

Photoelectron emission by an aqueous solution of the univalent anion  $A^-(aq)$  is the opposite of the hydration of the ion  $A^-(g)$  except that the negative charge is removed from solution by the emitted electron and the hydrated atom or radical  $A(aq)$  is left in solution in the case of emission. Solvation of anions and nuclear reorganization in photoionization therefore are closely related [1] (fig. 1). Solvation of  $A^-(g)$  is described as the formation of a cavity of radius  $r_i$  and the orientation of  $N_i$  solvent molecules in the inner-sphere region of  $A^-(aq)$ , e.g., in an octahedral configuration. There is also polarization of the outer-sphere region which is treated as a continuous medium. Emission involves the removal of the charge  $e^-(g)$  from the anion  $A^-(aq)$  to the gas phase and a change of the cavity radius from  $r_i$  to the value  $r_f$  corresponding to the atom or radical  $A$ .

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Subsequent nuclear reorganization changes the solvent configuration around  $A(aq)$  and, in some cases, the number of solvent molecules from  $N_i$  to  $N_f$ , e.g., from an octahedral to a tetrahedral configuration.

Two opposite approaches can be followed to calculate the energy of inner-sphere reorganization in photoionization. (i) The terms not corresponding to nuclear motion and the outer-sphere Born solvation term are subtracted from the experimental solvation energy. (ii) Only the terms pertaining to nuclear motion are retained in the theoretical expression for the solvation energy. The first approach used in [1] yields the reorganization energy as the difference between two quantities which are significantly larger than the energy being sought. The second approach adopted in the present paper neither has this disadvantage nor requires the knowledge of the solvation energy. A fairly standard model of ionic solvation [2] will be used.

The approach in this paper is similar in principle to that followed by Marcus [3] in his treatment of outer-sphere reorganization except that a multipole expansion of the inner-sphere potential is used instead of the continuous medium model for the outer-sphere region. The possibility is being examined of extending the present treatment to the calculation of the inner-sphere reorganization energy in the photoionization of metal cations and complexes. A bond-stretching model [4,5] is used at the present for these species under the conditions discussed in [1] in the case of photoionization.

## 2. Energy of inner-sphere reorganization of anions

Consider the photoionization of the univalent anion  $A^-(aq)$  in aqueous solution with the formation of the hydrated atom or radical  $A(aq)$ . In view of the discussion in sec. 1, the energy  $U_{IN}$  ( $> 0$ ) for inner-sphere reorganization may be written as

$$U_{IN} = U^f(\text{nuc1}) - U^i(\text{nuc1}), \quad (1)$$

where  $U^f(\text{nuc1})$  and  $U^i(\text{nuc1})$  represent, respectively, the terms in the expression of the hydration energies of  $A(\text{aq})$  and  $A^-(\text{aq})$  which correspond only to nuclear motion in the solvation of these species. The superscripts  $f$  and  $i$  in this and subsequent equations denote the species  $A(\text{aq})$  and  $A^-(\text{aq})$ , respectively. The term  $U^f(\text{nuc1})$  in eq. (1) represents the nuclear contribution to the solvation energy of the species  $A(\text{aq})$  surrounded by its equilibrium inner-sphere shell of solvent. Conversely,  $U^i(\text{nuc1})$  denotes the nuclear contribution from the species  $A(\text{aq})$  surrounded by the nonequilibrium inner-sphere solvent shell of the ion  $A^-(\text{aq})$ . Furthermore, the reorganization energy  $U_{IN}$  is determined by the change in ionic valence caused by photoionization and not by the absolute value of the ionic valences of the species involved in this process. Equation (1) is the counterpart of the expression for the free energy of orientation polarization in the treatment of outer-sphere reorganization on the basis of a continuous medium model [3].

The expression for  $U^i(\text{nuc1})$  is taken from [2] with the additional consideration of the difference in water orientation around anions and cations. By analogy with [2], one writes

$$U^f(\text{nuc1}) = U_{\text{disp}}^f + U_{\text{rep}}^f + U_v^f + U_c^f, \quad (2)$$

where  $U_{\text{disp}}^f$  is the London water-water dispersion energy;  $U_{\text{rep}}^f$  the Born water-water repulsion energy;  $U_v^f$  the energy corresponding to the volume change of the solvent upon hydration of  $A(\text{g})$ ;  $U_c^f$  the energy for cavity formation and the breaking up of the solvent structure in the hydration of  $A(\text{g})$ .

Combining eqs. (1) and (2) with the expression for  $U^i(\text{nuc1})$  from [2], one obtains

$$U_{IN} = -U^i(ep) - U^i(eq) - U^i(pp) - U^i(pq) - U^i(qq) - U_{disp}^i - U_{rep}^i - U_v^i - U_c^i + U_{disp}^f + U_{rep}^f + U_v^f + U_c^f, \quad (3)$$

where the first five terms on the right hand side represent interaction energies involving the change (e) of ionic charge upon photoionization, water permanent dipoles (p) and quadrupoles (q). The next four terms with superscript i in eq. (3) are analogous to the corresponding terms in eq. (2). Explicit forms except for the  $U_v$ 's and  $U_c$ 's are [2]

$$U^i(ep) = - (N_i e p / r_i^2) \cos \beta \quad (4)$$

$$U^i(eq) = N_i e \theta / 2 r_i^3 \quad (5)$$

$$U^i(pp) = (B p^2 / r_i^3) \cos^2 \beta \quad (6)$$

$$U^i(pq) = - (C p \theta / r_i^4) \cos \beta \quad (7)$$

$$U^i(qq) = D \theta^2 / r_i^5 \quad (8)$$

$$U_{disp}^i = - F_i I \alpha^2 / r_i^6 \quad (9)$$

$$U_{rep}^i = - (1/x) \{ 2U^i(ep) + 3[U^i(pp) + U^i(eq)] + 4U^i(pq) + 5U^i(qq) + 6U_{disp}^i \} \quad (10)$$

$$U_{disp}^f = F_f I \alpha^2 / r_f^6 \quad (11)$$

$$U_{rep}^f = - 6U_{disp}^f / x, \quad (12)$$

where  $N_i$  is the number of solvent molecules in the inner-sphere shell of  $A^-(aq)$ ;  $r_i$  the charge-point multipole distance, namely  $r_i = r_c + r_w$  ( $r_c$  and  $r_w$  crystallographic radii of  $A^-(g)$  and water, respectively);  $r_f = r_r + r_w$  ( $r_r$  the radius of  $A(g)$ );  $e$  the absolute value of the electronic charge;  $p$  the permanent dipole moment of water;  $\theta$  the quadrupole moment of water;  $\beta$  the angle between the vectors representing the electric field of the charge and the permanent dipole of the solvent;  $I$  the gas-phase ionization energy of water;  $\alpha$  the polarizability of water;  $x$  the exponent in the Born repulsion expression. The dimensionless coefficients B to F are [2,6]  $B = 2.296$



and 7.114; C = 1.722 and 5.336; D = 0.5490 and 2.030; F = 0.2373 and 1.160 for tetrahedral and octahedral configurations of the solvent molecules, respectively.

The quadrupole moment  $\theta$  of eqs. (5), (7), (8) was calculated by assuming that water molecules rotate freely about the OH-anion axis. The system of coordinates of [7] is defined as follows: the water molecule and the xz axes are represented as being in the plane of the paper; the positive segment of the z-axis bisects the HOH angle; the angles between the x- and z-axes and the OH-anion axis are  $\pi/2 - \beta$  and  $\beta$ , respectively. All the y-components of  $\theta$  are equal to zero in view of the assumption of free rotation of the water molecule about the OH-anion axis. Thus, one has  $\theta_{xz} = (\theta_{xx}^2 + \theta_{zz}^2)^{1/2}$  and the angle between  $\theta_{xz}$  and the OH-anion axis is  $\pi/2 - \beta + \cos^{-1} \theta_{xx}/\theta_{xz}$ . Hence,

$$\theta = (\theta_{xx}^2 + \theta_{zz}^2)^{1/2} \cos[\pi/2 - \beta + \cos^{-1} \theta_{xx}(\theta_{xx}^2 + \theta_{zz}^2)^{-1/2}], \quad (13)$$

where  $\theta_{xx} = 2.636 \times 10^{-26}$  and  $\theta_{zz} = -0.135 \times 10^{-26}$  esu cm<sup>2</sup> according to [7].

The energy  $U_v^i$  is according to [2]

$$U_v^i = - (v_{\text{eff}} - v_{\text{pm}}) / \beta_c, \quad (14)$$

where  $v_{\text{eff}}$  and  $v_{\text{pm}}$  are the effective and partial molar volume of the anion, respectively, and  $\beta_c$  is the compressibility of water. A negative sign is assigned to the right-hand-side of eq. (14) in the present treatment since the initial state corresponds to the solvated ionic species and thus differs from that of [2]. Data on these volumes are given in [8]. Actually, the right-hand-side of eq. (14) is equal to the free energy  $\Delta G_v^i$  rather than the energy, but this does not matter in view of the smallness of this term in eq. (3) (see numerical results below). The energy  $U_v^f$  for the atom or radical A(aq) was taken to be equal to zero.

The difference  $U_C^f - U_C^i$  in eq. (3) was obtained by noting that solvation of  $A(aq)$  for the halogens involves only the rotation of two of the four water molecules surrounding  $A(aq)$  without a net change of hydrogen bonds and with conservation of tetrahedral symmetry [9]. In contrast, the substitution of the halogen atom by the halide ion involves a change from tetrahedral to octahedral configuration and consequently the breaking of one hydrogen bond. The reverse process from ion to atom therefore involves the net formation of one hydrogen bond, i.e.,  $U_C^f - U_C^i = -0.27$  eV on the basis of the calculation in [2]. This analysis does not apply to the hydroxide ion since both this ion and the hydroxyl radical have the same number of hydrogen bonds [9,10]. Hence,  $U_C^f - U_C^i = 0$  for the photoionization of hydroxide ion.

The values of the energy  $U_{IN}$  from eq. (3) and the contributions to this energy are listed in table 1 with relevant data [11-14] for the photoionization of the halide and hydroxide ions. The charge-dipole term  $-U^i(ep)$  is dominant and the charge-quadrupole term in  $-U^i(eq)$  is very significant. The term  $\Delta U_C$  pertaining to hydrogen bonding is far from negligible for the halides. The other terms in table 1 are generally smaller in absolute value than the charge-dipole and charge-quadrupole terms or are even negligible. The charge-octopole term was not included because only terms in the electric field ( $r_i^{-2}$ ) and its first gradient ( $r_i^{-3}$ ) are significant ( $> kT$ ) in the multipole expansion according to [15] if the ion-point multipole distance is  $\geq 3$  Å.

### 3. Comparison with experimental free energies of inner-sphere reorganization

The free energy of reorganization can be computed from experimental threshold energies  $E_t$  for photoelectron emission by aqueous solutions of the anion being studied [16]. One has

$$E_t = \Delta G_H + \Delta G + R_{IN} + R_{OUT} + |e|\Delta x, \quad (15)$$

where  $\Delta G_H = 4.48$  eV;  $\Delta G$  is the change of free energy for the reaction  $A^-(aq) + H^+(aq) = A(aq) + 1/2H_2(g)$ ;  $\Delta x$  is the difference between the surface potentials of the solution of  $A^-(aq)$  and water. This last term is generally very small ( $< 0.05$  eV) and was neglected. The free energy  $R_{OUT}$  for the outer-sphere reorganization is [3]

$$R_{OUT} = (\epsilon_{op}^{-1} - \epsilon_s^{-1})e^2/2a, \quad (16)$$

where  $\epsilon_{op}$  ( $= 1.777$  at  $25^\circ C$ ) and  $\epsilon_s$  are the optical and static dielectric constants of water, respectively, and  $a = r_c + 2r_w$ .

Values of  $R_{IN}$  computed from eqs. (15) and (16) for the halide and hydroxide ions are listed in table 2 with supporting data. The threshold energies were obtained in earlier work [1,17] except for fluoride. The previously used glass cell and quartz rotating disk target were not suitable for fluoride solutions because the leaching of impurities under the action of the fluoride solution (5 M KF) resulted in strong spurious photoelectron emission at photon energies well below 10 eV. A plastic-lined cell and platinum rotating disk target were satisfactory but not easy to use because of difficulties in removing traces of low-energy photoelectron emitting impurities. Moreover, the photon flux above 10.5 eV was only 10 percent at most of the level prevailing at lower photon energies. The threshold energy  $E_t = 10.57$  eV was obtained (fig. 2) by extrapolation [16] after subtraction of the yield  $Y_{H_2O}$  for emission by water ( $E_t = 10.06$  eV) from the total yield for emission by water and fluoride ion. The yield  $Y_{H_2O}$  in the range of emission by fluoride ion was obtained by extrapolation above 10.6 eV the linear plot of  $Y_{H_2O}^{1/2}$  against photon energy observed below the threshold energy of fluoride ion. The linearity of the extrapolation plot for pure water was verified up to 11.0 eV. More accurate values of the change of

free energy are available for  $A^-(aq) + H^+(aq) = A(g) + 1/2H_2(g)$  for the halides [19], and the error on  $\Delta G$  in table 2 arises mostly from the uncertainty on the free energy of solvation of the halogen atoms.

Only the continuous medium model of the outer-sphere region enters into the computation of  $R_{OUT}$  in table 2. This model is reliable and not sensitive to the choice of  $r_c$ , and the values of  $R_{IN}$  thus obtained can be regarded as "experimental" data. These values are, of course, independent of any model for the inner-sphere region, but two sources of error on  $R_{IN}$  in table 2 must be noted: (i) the uncertainty of  $\pm 0.1$  eV on  $E_t$  resulting from the distortion of the extrapolation plot caused by the effect of dielectric dispersion on the energetics of photoionization [20]; (ii) the uncertainty of  $\pm 0.1$  eV on  $\Delta G$  arising from the estimation of the free energy of solvation of the halogen atoms and hydroxyl radical [9]. The first source of error affects especially the threshold energy of chloride ion, and values of  $E_t$  ranging from 8.8 to 9.0 eV are obtained depending on the extrapolation range of photon energies.

Agreement between the experimental free energies  $R_{IN}$  of table 2 and the calculated energies  $U_{IN}$  in table 1 is remarkably good for the halides. The entropy contribution to  $R_{IN}$  is probably within the experimental error (see above). The rather good agreement for the hydroxide ion also shows that the spherical symmetry of the ion, which prevails for the halide ions, is not absolutely essential to the application of the present theoretical calculations.

#### Acknowledgment

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Table 1

Contributions to the inner-sphere reorganization energy of the halide and hydroxide ions in eq. (3)<sup>a)</sup>

Anion	$-U^i(\text{ep})$ (ev)	$-U^i(\text{eq})$ (ev)	$-U^i(\text{pp})$ (ev)	$-U^i(\text{pq})$ (ev)	$-U^i(\text{qq})$ (ev)	$-\Delta U_{\text{disp}}$ (ev)	$\Delta U_{\text{rep}}$ (ev)	$\Delta U_{\text{v}}$ (ev)	$\Delta U_{\text{c}}$ (ev)	$U_{\text{IN}}$ (ev)
$\text{F}^-$	2.72	-0.87	-0.28	0.13	-0.03	-0.01	-0.18	0.21	-0.27	1.42
$\text{Cl}^-$	2.01	-0.55	-0.18	0.07	-0.02	-0.01	-0.16	0.05	-0.27	0.94
$\text{Br}^-$	1.84	-0.49	-0.16	0.06	-0.01	0.00	-0.16	0.03	-0.27	0.84
$\text{I}^-$	1.63	-0.41	-0.13	0.05	-0.01	0.00	-0.15	0.00	-0.27	0.71
$\text{OH}^-$	1.68	-0.52	-0.08	0.04	-0.01	0	-0.14	0.27	0	1.24 <sup>c)</sup>

a)  $N_i = 6$  from  $\text{F}^-$  to  $\text{I}^-$  according to neutron diffraction results [11,12],  $N_i = 4$  for  $\text{OH}^-$  [9].  $N_f = 4$  for halogen atoms and hydroxyl radical. Radii from  $\text{F}^-$  to  $\text{OH}^-$ :  $r_i = 1.36, 1.81, 1.95, 2.16, 1.47 \text{ \AA}$  [13];  $r_f = 0.68,$

0.97, 1.13, 1.35, 1.47  $\text{\AA}$  (see [14] for OH). Other data:  $\beta = 52.23^\circ$  [11,12];  $x = 12$  for anions and  $x = 10$  for halogen atoms and OH radical [10];  $p = 1.854$  debyes,  $\alpha = 1.444 \times 10^{-24} \text{ cm}^3$ ,  $I = 12.61 \text{ eV}$ .

b)  $\Delta U = U^f - U^i$  for the four  $\Delta U$ 's.

c) Negligible contribution from vibration of OH since the O-H distance is the same for  $\text{OH}^-$  and OH within 0.002  $\text{\AA}$  [14].

Table 2

Free energies  $R_{IN}$  for inner-sphere reorganization from experimental threshold energies

Anions	$E_t$ <sup>a)</sup> (eV)	$\Delta G$ <sup>b)</sup> (eV)	$R_{OUT}$ (eV)	$R_{IN}$ (eV)
$F^-$	10.6	3.6	0.96	1.56
$Cl^-$	8.9	2.55	0.87	1.00
$Br^-$	8.15	2.0	0.84	0.83
$I^-$	7.4	1.4	0.80	0.72
$OH^-$	8.6	1.8	0.94	1.38

<sup>a)</sup> From refs. [1] and [17].

<sup>b)</sup> From ref. [9] except for  $OH^-$  [18]. See text for comments on  $\Delta G$ .

## Captions to Figures

Fig. 1. Solvation, photoelectron emission from the anion and nuclear reorganization for a univalent  $A^-$  in aqueous solution. Cavity radii  $r_i$  and  $r_f$  for  $A^-(aq)$  and  $A(aq)$ , respectively;  $N_i$  and  $N_f$  solvent molecules in the inner-sphere shell of  $A^-(aq)$  and  $A(aq)$ , respectively. The shaded area represents the outer-sphere region.

Fig. 2. Extrapolation plot for the determination of the threshold energy of fluoride ion for 5 M KF in aqueous solution. See text for the determination of the yield  $Y_{F^-}$  of fluoride ion from the measured yield.



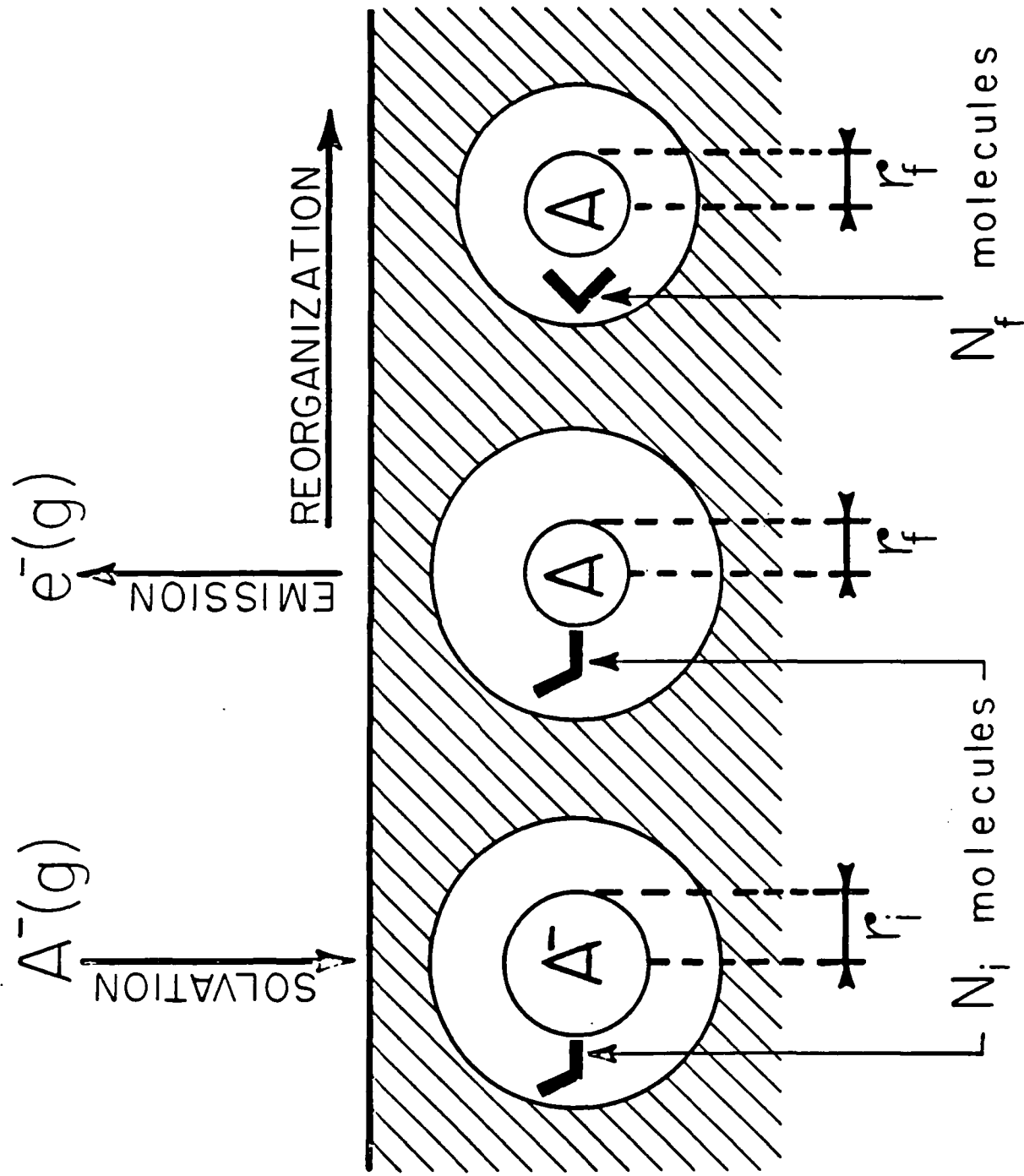


FIG. 1

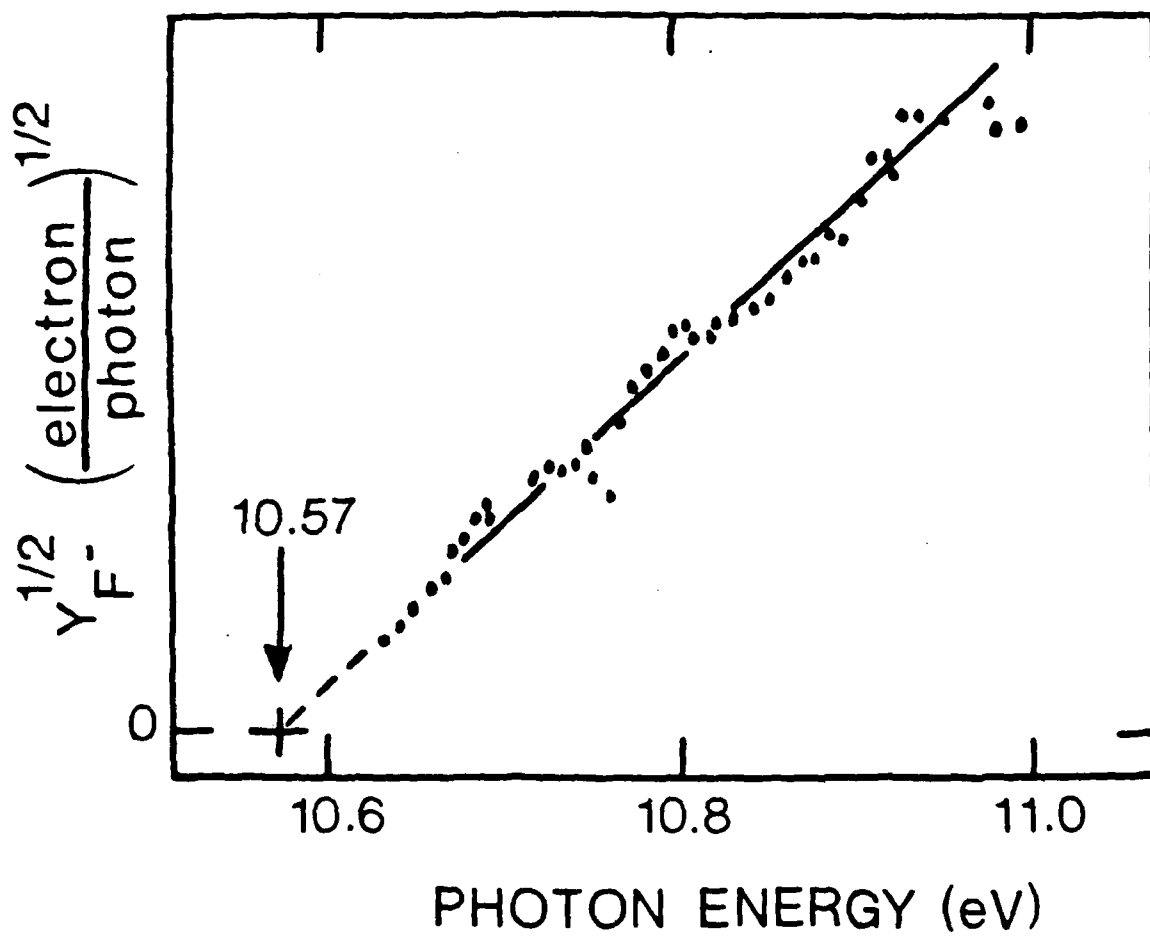


FIG. 2

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